PORTLAND HARBOR RI/FS

APPENDIX B

FOOD WEB MODEL DEVELOPMENT FOR PORTLAND HARBOR AQUATIC SYSTEMS

FEASIBILITY STUDY

DRAFT

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LIST OF ACRONYMS

BAF	bioaccumulation factor
COC	contaminant of concern
FWM	Food Web Model
GI	gastrointestinal tract
K_{ow}	octanol-water partition coefficient
LWG	Lower Willamette Group
ng/L	nanograms per liter
NLOM	non-lipid organic matter
PAHs	polycyclic aromatic hydrocarbons
PCBs	polychlorinated biphenyls
PRGs	Preliminary Remediation Goals
RI/FS	Remedial Investigation/Feasibility Study
µg/kg dw	microgram per kilogram dry weight
USEPA	U.S. Environmental Protection Agency
ww	wet weight

EXECUTIVE SUMMARY

This appendix provides a description of the process utilized to develop a food web model (FWM) for the Portland Harbor Superfund Site.

1.0   FOOD WEB MODEL DEVELOPMENT BACKGROUND

The Lower Willamette Group (LWG) developed a modeling approach to assist with developing sediment Preliminary Remediation Goals (PRGs) based on protection of upper trophic-level ecological receptors, illustrating uncertainties in these PRGs, and estimating risk reduction for various remedial alternatives. The model was also used to help establish appropriate sediment PRGs for protection of people that may take and consume fish and shellfish from the lower Willamette River, and to assess risk reduction. The Food Web Model (FWM) has not been summarized in a single location to date, and understanding of function and use of this model currently is described in several LWG documents submitted to, but not approved, by the U.S. Environmental Protection Agency (USEPA). This report provides a succinct description of the model. Previous draft reports can be consulted to understand how the model was chosen and adapted to Portland Harbor.

The FWM chosen for use in the Portland Harbor Remedial Investigation/Feasibility Study (RI/FS), the Arnot and Gobas (2004) model, was judged to be the better predictor of empirical tissue concentrations (Windward Environmental 2005). The model uses a series of calculations to estimate accumulation of persistent organic chemicals for physical media (sediment and surface water) to tissues of predatory fish. Elements of these calculations are described in the following sections.

1.1   FOOD WEB MODEL COMPONENTS

The Arnot and Gobas model was used to simulate transfer of persistent organic chemicals from surface water and sediment through a series of biological compartments represented by generic groups (e.g., phytoplankton), trophic levels (foraging fish), and specific species (smallmouth bass). Compartments included in the model are:

- Phytoplankton

- Zooplankton

- Benthic infaunal filter feeders (clams, *Corbicula fluminea*)

- Benthic infaunal consumers (oligochaetes, insect larvae and amphipods)

- Epibenthic invertebrate consumers (crayfish, no species identified)

- Foraging fish (sculpin, *Cottus* sp) (Group also used to represent black crappie [*Pomoxis nigromaculatus*] and peamouth [*Mylocheilus caurinus*])

- Benthivorous fish (largescale sucker, *Catostomus macrocheilus*) (Group also used to represent brown bullhead [*Ameiurus nebulosus*])

- Omnivorous fish (common carp, *Cyprinus carpio*)

- Small piscivorous fish (smallmouth bass, *Micropterus dolomieui*)

- Large piscivorous fish (Northern Pikeminnow, *Ptycholcheilus oregonenesis*)

1.2   FOOD WEB MODEL CALCULATIONS - OVERVIEW

The Arnot and Gobas model in its most general form will estimate the change in mass of chemicals in an organism over time, based on (1) uptake of chemicals in water across respiratory surfaces (gills/integument) or, following ingestion, in water and food from the gastrointestinal tract (GI), and (2) elimination from respiratory surfaces, in urine, and in feces. Metabolism is included as an elimination process, but has limited importance for poorly metabolized chemicals such as polychlorinated biphenyls (PCBs). For readily metabolized chemicals, such as polycyclic aromatic hydrocarbons (PAHs), metabolism may be a dominant process controlling accumulation in tissues.

The model requires estimation or measurement of a large number of input parameters (**Table B-1**). These parameters are used in a set of interconnected equations to provide estimates of concentrations of chemicals in species that represent several trophic guilds in the food web, as noted above. The model developed for Portland Harbor used the same seven trophic guilds as proposed by Arnot and Gobas – primary producers; zooplankton and pelagic invertebrates; benthic invertebrates; water column filter feeders; and small (juvenile), medium-sized and larger upper trophic level fish. However, an epibenthic invertebrate guild (crayfish) was added and five fish species – sculpin, largescale sucker, common carp, smallmouth bass and northern pikeminnow – were modeled within the three size categories for fish to account for differences in feeding behavior. Thus, a total of 10 trophic guilds were included in the model.

The general form of the model was simplified for practical reasons to predict chemical concentrations at a single point in time (assumed to be steady state), as shown in Equation 1 below.

Equation 1 is the general form of the Arnot and Gobas model, and is explained in more detail in subsequent sections. The model estimates concentrations of non-ionic organic chemicals in an aquatic organism (C_b). In the form provided, the model estimates chemical concentrations via uptake and elimination of chemicals present in water, sediment, and diet assuming steady-state conditions. This assumption is reasonable where (a) organisms are exposed for long periods of time, (b) exchange kinetics are rapid relative to time of exposure, and (c) sources of chemicals in abiotic media are stable relative to the time of exposure. Typically, the model predicts best when estimating concentrations for chemicals with an octanol-water partition coefficient (K_{ow}) less than $10^{7.5}$ and for small organisms that achieve steady-state rapidly (e.g., phytoplankton, insect larvae, etc.). For larger organisms (e.g., smallmouth bass, carp), growth is assumed to be adequately modeled as a constant fractional increase in body weight over time (k_G).

Chemical partitioning between water and organism (k_1/k_2), and ingestion (diet) and subsequent uptake in the GI tract (k_D/k_E), determine steady-state chemical concentrations, though as mentioned above, metabolism may play a critical role for some chemicals/chemical groups. For primary producers, k_D and k_E are 0. Although some elimination of chemicals from phytoplankton, algae, and macrophytes may occur, it is assumed to be insignificant.

$$C_b = \{k_1 * (m_O * \phi * C_{WT,O} + m_p * C_{WD,S}) + k_D * \sum P_i * C_{D,i}\}/(k_2 + k_E + k_G + k_M) \quad (1)$$

Where:

C_b – chemical concentration in organism

k_1 – rate constant for gill/skin uptake from water

m_O – fraction of gill/skin uptake from surface water

m_p – fraction of gill/skin uptake from transition zone/pore water

ϕ – dissolved fraction of chemical in surface water

$C_{WT,O}$ – chemical concentration in surface water

$C_{WD,S}$ – dissolved fraction of chemical in transition zone/pore water

k_D – rate constant for uptake from GI tract

P_i – fraction of diet for food item i

$C_{D,i}$ – chemical concentration in food item i

k_2 – rate constant for elimination from gill/integument[1]

k_E – rate constant for elimination in feces

k_G – growth rate constant

k_M – rate constant for chemical metabolism

The model does not partition chemicals within organisms (i.e., into various organs and tissues). Comparisons of predicted and empirical concentrations for poorly metabolized chemicals suggest that such detail is not needed for most applications. For example, smallmouth bass will consume whole prey, and relative mass of chemical in organs of prey is not likely to be important relative to kinetics of uptake in the GI tract.

Equation 1 is used multiple times in modeling trophic transfer. For example, C_b calculated for crayfish will subsequently be substituted C_D in Equation 1 to represent the concentration of chemical for the fraction of diet for a predator that is represented by crayfish. The full model, therefore, is a series of Equation 1 calculations that feed into one another starting with primary producers and ending with the highest trophic guild predators. For each calculation, parameters appropriate for the trophic guild are input to the calculations, and the previous $C_b(s)$ used to represent dietary constituents for that guild.

1.3   MODEL CALCULATIONS – DETAILED DESCRIPTION

Parameters in Equation 1 generally must be themselves estimated from data collected during field activities or from information taken from the literature. As examples, estimates of surface water and transition zone/pore water must be estimated from measurements made in the field. Similarly, uptake of chemicals in water requires

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[1] Integument is used generically to include uptake across the skin and uptake into primary producers (phytoplankton, algae, and macrophytes). Skin is not evaluated in the model as an active respiratory surface for the species included in the several trophic guilds.

estimates from the literature on ventilation rates for gill surfaces of different fish species. Before C_b can be calculated, several subcalculations are necessary to identify input to the basic equation. These calculations are described briefly below, and equations provided in **Table B-3**. Individual parameters and their values used in the FWM are separately described (**Table B-1**).

In the discussion below, some equations most important for a conceptual understanding of the FWM are repeated in the text to help ensure clarity. In most cases, text refers back to **Table B-3** for equations used in the model.

1.3.1   Phase Partitioning

Partitioning of lipophilic chemicals into organisms occurs into lipid, non-lipid organic matter (NLOM), and water. Often, partitioning into lipid dominates uptake of chemicals such as PCBs. However, for organisms with low lipid content such as phytoplankton, partitioning into non-lipid organic matter can play an important role in controlling partitioning. To account for partitioning, a variable (K_{BW}) is defined for each organism (Equation 2).

$$K_{BW} = \frac{k_1}{k_2} = v_{LB} * K_{OW} + v_{NB} * \beta * K_{OW} + v_{WB} \quad (2)$$

Where:

v_{LB} = lipid fraction (ww)
K_{OW} = octanol/water partition coefficient
v_{NB} = non-lipid fraction (ww)
β = proportionality constant (sorption capacity of NLOM relative to lipid)
v_{WB} = water fraction

Lipophilic chemicals have a substantial affinity for organic matter in water and sediment. A chemical that is bound to organic matter is generally not available for uptake into organisms. Binding to organic matter is therefore an important controlling factor in determining the fraction of chemical that is bioavailable. A variable (ϕ) is defined to express the fraction of freely dissolved chemical in either surface or transition zone/pore water (Equation 3).

$$\phi = \frac{c_{WD}}{c_{WT}} = 1/(1 + \chi_{POC} * D_{POC} * \alpha_{POC} * K_{OW} + \chi_{DOC} * D_{DOC} * \alpha_{DOC} * K_{OW}) \quad (3)$$

Where:

$\frac{c_{WD}}{c_{WT}}$ = dissolved concentration in water/total concentration in water

χ_{POC} = concentration of particulate organic matter in water

D_{POC} = disequilibrium factor[2] for particulate organic matter in water

α_{POC} = proportionality constant (partitioning of chemical into POC relative to octanol)

χ_{DOC} = concentration of dissolved organic matter in water

D_{DOC} = disequilibrium factor for dissolved organic matter in water

α_{DOC} = proportionality constant (partitioning of chemical into DOC relative to octanol)

1.3.2   Rate Constants

Several rate constants used in Equations 1 through 3 require additional calculations. These calculations are described below and equations provided in **Table B-3**.

k_1 and k_2

These constants estimate the rate at which chemicals are absorbed across gills/integument. They are expressed as uptake clearance constants in units of L/kg-d. For fish, invertebrates and zooplankton, k_1 is estimated as a function of ventilation rate (G_v), diffusion rate (E_w) and organism wet weight (W_B) (**Table B-1**, Equation 4). Ventilation rate is estimated using an allometric relationship from the literature based on oxygen consumption and wet weight (W_B) (**Table B-3**, Equation 5). Oxygen concentration (C_{ox}) in water is estimated based on thermodynamics as a function of temperature (C_{ox} = (-0.24*T+14.04)*S, where T is temperature in degrees Celsius (°C) and S is percent oxygen saturation (**Table B-3**, Equation 6). Diffusion rate (or uptake efficiency) is estimated from the literature as a function of K_{ow} (**Table B-3**, Equation 7).

For primary producers, k_1 is estimated as a function K_{ow} and two constants (A and B) that express resistance to uptake through aqueous and organic phases, respectively (**Table B-3**, Equation 8). Values for A and B are derived from the literature.

Estimates for k_2 are calculated as k_1/K_{BW} (**Table B-2**, Equation 9), since k_2 depends on the same factors as k_1. For primary producers, calculation of K_{PW} (partition coefficient for primary producers and water) is calculated by substituting NLOM in Equation 2 with

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[2] Disequilibrium factors greater than one suggest binding in excess of partition coefficient and factors less than one indicate that equilibrium has not been reached. Disequilibrium is observed in the field, but quantification is difficult. Proportionality constants are also observed empirically to vary significantly depending on the source of organic carbon. These input parameters are estimated separately for each chemical included in the model (Table 3).

non-lipid organic carbon (ww) (**Table B-3**, Equation 10). Note that bioaccumulation factor (BAF) is the ratio of k_1 to k_2. Since these rates depend on the same factors, exact determination of parameters G_v and E_w is not necessary. Any error introduced into the estimate of k_1 will be countered by a similar error in k_2.

m_o and m_p

These parameters represent the fraction of chemical taken up across the gill for surface and pore water, respectively. Pore water may be an important source of chemicals to the food web via organisms that have intimate contact with sediments (e.g., benthic macroinvertebrates, common carp). Chemicals in pore water may be important for uptake of chemicals into the food web. Such situations occur when surface water is not in equilibrium (i.e., D_{doc} is less than 1), but pore water is at least in equilibrium (i.e., D_{doc} is 1 or greater). Values for m_p derived from the literature for organisms with sediment contact are used in the model. For organisms with little or no close contact with sediment, m_p is zero. In all cases, $m_o = 1 - m_p$.

k_D and k_E

Rate constant for absorption of chemical from diet (k_D) is expressed as an uptake clearance rate and is a function of transfer efficiency (E_D), feeding rate (G_D), organism weight (W_B) and temperature (T) (**Table B-3**, Equation 11). Values for E_D vary between 0 and 100 percent across species and chemicals. However, reasonable estimates can be obtained from **Table B-3**, Equation 12:

$$E_D = (3 \ x \ 10^{-7} * K_{ow} + 2)^{-1}$$

Feeding rate (G_D) is also a variable, but can reasonably be approximated based on energy requirements for fish, zooplankton, and some other invertebrates (**Table B-3**, Equation 13). A separate equation is needed for filter feeders (e.g., clams) because the food intake is a function of the gill ventilation rate (**Table B-3**, Equation 14).

The rate constant for elimination from the organism (k_E) is a function of fecal excretion (**Table B-3**, Equation 15). Elimination is a function of G_F – the ratio of fecal weight to organism weight, E_D, partitioning between organism, and GI tract (K_{GB}) (**Table B-3**, Equation 16) and body weight (W_B). G_F in this equation is a function of both dietary content (v_{LD}, v_{ND}, v_{WD}) and dietary assimilation constants (ε_L, ε_N, ε_W) for lipid, NLOM, and water, respectively (**Table B-3**, Equation 17).

Partitioning across the GI tract to organism (K_{GB}) captures changes in phase partitioning that results from digestion of food. The parameter is estimated as a function of fraction of total digested represented by lipid, NLOM, and water (v_{LG}, v_{LN} , v_W). These parameters are estimated from assimilation efficiency for each component of the diet (**Table B-3**, Equations 18 - 20).

Note that BAF is based on the ratio of k_D to k_E (G_D/G_F*K_{GB}). Errors for feeding rate and dietary uptake efficiency (G_D and E_D) thus tend to cancel out to a large degree. BAF estimates from the model can still be reasonable even where feeding rate and dietary uptake efficiency are not well characterized. Since such errors are potentially large, this aspect of the model significantly increases its utility. Note also that variability in dietary uptake of chemicals characterized by high-K_{ow} can also be large, but typically substantially smaller than variability in G_D and E_D.

k_G

The literature is relatively rich with estimates of growth rates for various species. Still, variability within species is high because of the influence of temperature, habitat, food availability, etc. An empirical allometric equation is used as a reasonable approximation of growth rate for different temperatures (**Table B-3**, Equation 21).

k_M

Metabolism of chemicals is dependent on both species-specific biochemical processes and chemical characteristics. Sufficient data to estimate k_M are often lacking, particularly for biological properties. k_M can reasonably be assumed to be zero for chemicals that are poorly metabolized (e.g., PCB and DDx[3]). However, for the Portland Harbor model, estimates of k_M where identified in the calibration process is described below.

1.3.3   Other Input Parameters

$C_{WD,P}$

Dissolved chemical concentrations in pore water are estimated as $C_{S,oc}*\delta_{ocs}/K_{oc}$, (**Table B-3**, Equation 22) where $C_{S,oc}$ is the sediment concentration normalized for organic carbon content of sediment, δ_{ocs} is density of organic carbon in sediment, and K_{oc} is the organic carbon – water partition coefficient.

$C_{S,oc}$

Organic carbon normalized chemical concentrations in sediment is simply the ratio of total chemical concentration to sediment organic carbon and is estimated simply as $C_{S,oc}/OC_{sed}$, (**Table B-3**, Equation 23) where $C_{S,oc}$ is total sediment concentration and OC_{sed} is percent organic carbon in sediment.

1.4   FWM CALIBRATION

Additional development of the Arnot and Gobas FWM for Portland Harbor focused on calibration of the model to empirical fish tissue data collected during Round 1 and Round 2 field investigations (Windward Environmental 2009). Calibration involved replacing single values for many input parameters with distributions that reflect a reasonable range of values. The model was then run many times, with each run selecting input parameters

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[3] The total of 2,4'- and 4,4'-DDD (dichloro-diphenyl-dichloroethane), -DDE (dichloro-diphenyl-dichloroethene), and -DDT (dichloro-diphenyl-trichloroethane).

randomly from input distributions[4]. Results of these runs were used to identify combinations of input parameters[5] that appeared to minimize differences between empirical and predicted PCB concentrations across all trophic levels. This approach did not yield a unique solution – that is, several different combinations of input parameters would yield reasonable fit to empirical data. This issue is further addressed below.

The calibration exercise emphasized the use of site-specific information as much as possible. Input distributions for the calibration exercise were developed using the following criteria:

- If site-specific data were available, estimates of mean and standard error were used to define a normal distribution. Water temperature is an example of an input parameter distribution defined using site data.

- If site data were lacking, but mean and standard deviation estimates were available in the literature, these estimates were used to define a normal distribution.

- For chemicals and chemical groups, uniform distributions were used to define log K_{ow} using data from the literature. For PCBs, site-specific data for congener composition of total PCBs was also considered to account for chemical differences among congeners.

- Triangular and uniform distributions were used for parameters for which mean and standard error/deviation estimates were not available. In most cases, defining these distributions involved consideration of values used in other published models and on professional judgment.

- For a number of parameters, point estimates were retained.

Although distributions for many input parameters were assigned[6], a sensitivity analysis that accompanied multiple model runs identified only a few parameters important in determining model fit to empirical data:

- Concentration of contaminant of concern (COC) in sediment solids (microgram per kilogram dry weight [µg/kg dw])

- Concentration of COC in surface water (nanogram per liter [ng/L], filtered)

- Log K_{ow}

- Water temperature (°C)

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[4] This approach is often referred to as a stochastic or "Monte Carlo" analysis.

[5] Calibrated inputs were single values for model parameters that reasonably reproduced empirical data from Round 1 and 2 field efforts. Tissue data from Round 3 was not subsequently used when they became available, since they were not collected in a manner that would yield representative sampling of the aquatic fish community. Round 3 tissue data do not, however, appear in general to be similar to data used to calibrate the FWM.

[6] Not all input parameters were assigned distributions for the calibration exercise. In these instances, fixed input parameters were used during model calibration.

- Benthic invertebrate consumer lipid content (%)

These parameters are either defined by site-specific data, or are well studied in the literature. Thus, confidence that calibrated parameters reasonably account for uncertainties in the model is relatively high. That is, manipulating inputs within reasonable ranges would, for most parameters, have little impact on model performance. Uncertainty due to choice of calibrated input parameters appears to be acceptable, given the assumption that fish tissue data are representative is appropriate.

An example of output from the calibrated FWM is provided as **Figure B-1**, which shows predicted (modeled) versus empirical data from the RI database.

After calibration, the FWM was linked to a fate and transport model to enhance the ability of the model to provide estimates for C_b over time. This "dynamic bioaccumulation model" is described separately. Supporting documentation for the FWM is included in the Windward (2009) draft report. Note that this report has not received approval from EPA.

2.0   REFERENCES

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Tables

Figures